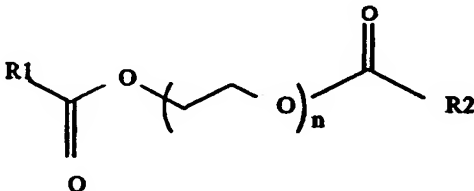


PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C11D 1/74, 3/37, 1/72</p>	<p>A1</p>	<p>(11) International Publication Number: WO 99/20724 (43) International Publication Date: 29 April 1999 (29.04.99)</p>
<p>(21) International Application Number: PCT/US98/21677 (22) International Filing Date: 14 October 1998 (14.10.98) (30) Priority Data: 97870160.5 22 October 1997 (22.10.97) EP (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): GORDON, Neil, James [GB/BE]; Van Elewijckstraat 107, B-1853 Strombeek-Bever (BE). EVERS, Marc, François, Théophile [BE/BE]; Lakensestraat 37, B-1853 Strombeek-Bever (BE). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).</p>		<p>(81) Designated States: CA, JP, MX, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: LIQUID HARD-SURFACE CLEANING COMPOSITIONS</p> <p>(57) Abstract</p> <p>Liquid hard-surface cleaning compositions are disclosed which provide outstanding next-time cleaning performance to the hard-surfaces cleaned therewith. The compositions comprise a polyalkoxyethylene glycol diester according to formula (I) wherein the substituents R₁ and R₂ each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chains having from 1 to 36 carbon atoms and wherein n is an integer from 10 to 400, and a vinylpyrrolidone homopolymer or copolymer.</p> <div style="text-align: center;">  <p>(I)</p> </div>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Liquid Hard-Surface Cleaning Compositions

5

Technical Field

The present invention relates to liquid compositions for cleaning hard-surfaces.

10

Background of the invention

Liquid compositions for cleaning hard-surfaces have been disclosed in the art. Much of the focus for such compositions has been on providing outstanding cleaning on a variety of surfaces and soils. However, such compositions are not fully satisfactory from a consumer viewpoint, especially regarding the soil release properties imparted to the hard-surfaces treated therewith. Indeed, consumers are looking for liquid cleaning compositions, whereby next-time (subsequent) cleaning is more facilitated.

The object of the present invention is to formulate a liquid cleaning composition for removal of various soils from hard-surfaces, that will facilitate the next-time cleaning operation.

It has now been found that the next-time cleaning performance is improved when a hard-surface has first been treated with a liquid composition comprising particular antiresoiling ingredients, namely a polyalkoxyene glycol diester as defined herein, as a first antiresoiling ingredient, together with a vinylpyrrolidone homopolymer or copolymer, as a second antiresoiling ingredient. Indeed, the compositions of the present invention allow improved next-time cleaning performance, as compared to the same compositions comprising only one of said antiresoiling ingredients as defined herein, at the same total level of antiresoiling ingredients, or another antiresoiling polymeric ingredient like for example poly (trimethyl aminoethyl) methacrylate at the same total level of antiresoiling ingredients.

More particularly, it has surprisingly been found that the use of such a polyalkoxyene glycol diester, as defined herein, together with such a vinylpyrrolidone homopolymer or copolymer, such as a quaternized or

unquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymer, results in a synergistic effect on next-time cleaning performance.

5 Advantageously, the compositions herein may be used to clean hard-surfaces made of a variety of materials like glazed and non-glazed ceramic tiles, vinyl, no-wax vinyl, linoleum, melamine, glass, plastics, plastified wood, both in neat and diluted conditions, e.g., up to a dilution level of 1:400 (composition:water).

10 A further advantage of the present invention is that the next-time cleaning performance is obtained with the compositions according to the present invention on various types of stains/soils including typical greasy stains like kitchen grease and other tough stains such as burnt/sticky food residues typically found in kitchens, while delivering good gloss to said surfaces.

15 Another advantage associated to the compositions according to the present invention comprising the polyalkoxyethylene glycol diester and vinylpyrrolidone homopolymer or copolymer, is that they have the ability to provide good shine to the surface they have cleaned. Indeed, less formation of watermarks and/or even limescale deposits are observed on a surface having been cleaned with
20 the compositions of the present invention and later comes in contact with water, for example, during a rinse operation. Advantageously, the shine benefit delivered to the surface even persists after several cycles of rinsing, thus providing long lasting protection against formation of watermarks and/or even limescale deposits on the surface, and hence long lasting shiny surfaces.

25 Another advantage of the liquid compositions of the present invention is that not only next-time cleaning performance is improved, but that also good first time cleaning performance is delivered. Yet a further advantage of the compositions of the present invention is that faster drying is obtained on the surfaces that have been cleaned therewith, this both when used diluted or when used neat.
30 In other words, the housewife will have the advantage to shorten the total time of the cleaning operation of hard-surfaces and diminish the inconvenience of having wet floors in her home.

WO 94/26858 discloses a liquid hard-surface composition (pH 2-8) with nonionic surfactants (1-30%) and anionic polymers having an average molecular weight of less than 1,000,000, said polymers being free of quaternary nitrogen groups. Said compositions bring initial cleaning benefit in addition to the anti-soiling benefit. Indeed, WO 94/26858 discloses that acrylic, methacrylic and maleic anhydride derivatives such as copolymers of styrene with maleic produce a streak-free finish after drying. No liquid compositions comprising a combination of a polyalkoxyethylene glycol diester together with a vinylpyrrolidone homopolymer or copolymer are disclosed.

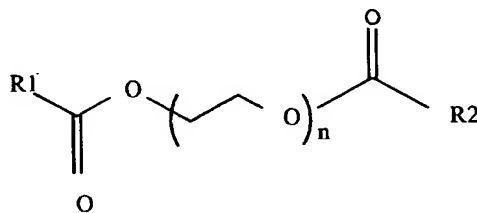
EP-A-635 567 discloses liquid compositions for cleaning solid surfaces comprising a cleaning agent capable of being deposited on the surface during cleaning and of forming a dried layer adhered to the surface, said layer having a cohesive strength such that at least outermost surface portion of the layer is removable by further washing. Polyvinylpyrrolidone is disclosed. However, no polyalkoxyethylene glycol diesters are disclosed.

20

Summary of the invention

The present invention encompasses a liquid hard-surface cleaning composition comprising a polyalkoxyethylene glycol diester according to the formula:

25



wherein the substituents R₁ and R₂ each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chains having from 1 to 36 carbon atoms and wherein n is an integer from 10 to 400, and a vinylpyrrolidone homopolymer or copolymer.

The present invention also encompasses a process of cleaning hard-surfaces wherein a liquid composition as defined herein above, is contacted with said surfaces.

5

Detailed Description of the invention

10

The liquid compositions:

15

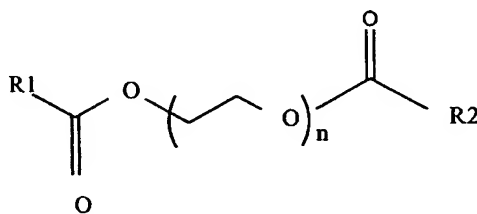
As a first essential ingredient, the compositions according to the present invention comprise a polyalkoxyethylene glycol diester or a mixture thereof, as defined herein after.

20

Typically, the compositions of the present invention comprise from 0.001% to 20% by weight of the total composition of said polyalkoxyethylene glycol diester or a mixture thereof, preferably from 0.01% to 10%, more preferably from 0.1% to 5% and most preferably from 0.2% to 2%.

Suitable polyalkoxyethylene glycol diesters for use herein have the following formula :

25



30

In this formula the substituents R_1 and R_2 each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chains having from 1 to 36 carbon atoms, and n is an integer of from 10 to 400.

Preferably R_1 and R_2 each independently are substituted or unsubstituted, linear or branched alkyl groups or alkenyl groups having from 1 to 36 carbon

atoms, preferably from 1 to 30, more preferably from 1 to 24, even more preferably from 1 to 22 and most preferably from 1 to 18, or aryl groups having up to 36 carbon atoms, preferably from 6 to 36, more preferably from 6 to 30. Preferably n is an integer from 20 to 400, more preferably from 40 to 300, even more preferably from 40 to 200 and most preferably from 40 to 150.

The preferred polyalkoxyethylene glycol diesters for use according to the present invention have a molecular weight of at least 200, more preferably from 400 to 10,000 and most preferably from 800 to 6,000.

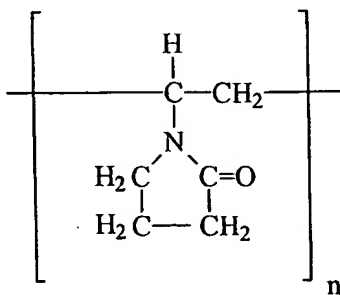
Suitable polyalkoxyethylene glycol diesters for use herein include O'O-distearyl polyethylene glycol diester (MW 6000) or O'O-dioleyl polyethylene glycol diester (MW 560).

Such polyalkoxyethylene glycol diesters may be commercially available from Akzo Nobel under the name KESSCO PEG 6000DS®, or from Lonza under the name Pegosperse® or from Huls under the name Marlosol FS®.

As a second essential ingredient, the compositions according to the present invention comprise a vinylpyrrolidone homopolymer or copolymer or a mixture thereof.

Typically, the compositions of the present invention comprise from 0.001% to 20% by weight of the total composition of a vinylpyrrolidone homopolymer or copolymer or a mixture thereof, preferably from 0.01% to 10%, more preferably from 0.1% to 5% and most preferably from 0.2% to 2%.

Suitable vinylpyrrolidone homopolymers for use herein is an homopolymer of N-vinylpyrrolidone having the following repeating monomer:



wherein n (degree of polymerisation) is an integer of from 10 to 1,000,000 preferably from 20 to 100,000, and more preferably from 20 to 10,000.

- 5 Accordingly, suitable vinylpyrrolidone homopolymers ("PVP") for use herein have an average molecular weight of from 1,000 to 100,000,000 , preferably from 2,000 to 10,000,000 , more preferably from 5,000 to 1,000,000 , and most preferably from 50,000 to 500,000.
- 10 Suitable vinylpyrrolidone homopolymers are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15® (viscosity molecular weight of 10,000), PVP K-30® (average molecular weight of 40,000), PVP K-60® (average molecular weight of 160,000), and PVP K-90® (average molecular weight of 360,000). Other
- 15 suitable vinylpyrrolidone homopolymers which are commercially available from BASF Cooperation include Sokalan HP 165® and Sokalan HP 12®; vinylpyrrolidone homopolymers known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).
- 20 Suitable copolymers of vinylpyrrolidone for use herein include copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers or mixtures thereof.

The alkylenically unsaturated monomers of the copolymers herein include unsaturated dicarboxylic acids such as maleic acid, chloromaleic acid, fumaric

25 acid, itaconic acid, citraconic acid, phenylmaleic acid, aconitic acid, acrylic acid, N-vinylimidazole and vinyl acetate. Any of the anhydrides of the unsaturated acids may be employed, for example acrylate, methacrylate. Aromatic monomers like styrene, sulphonated styrene, alpha-methyl styrene, vinyl toluene, t-butyl styrene and similar well known monomers may be used.

30

The molecular weight of the copolymer of vinylpyrrolidone is not especially critical so long as the copolymer is water-soluble, has some surface activity and is adsorbed to the hard-surface from the liquid composition or solution (i.e. under dilute usage conditions) comprising it in such a manner as to increase the

35 hydrophilicity of the surface. However, the preferred copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers or mixtures thereof,

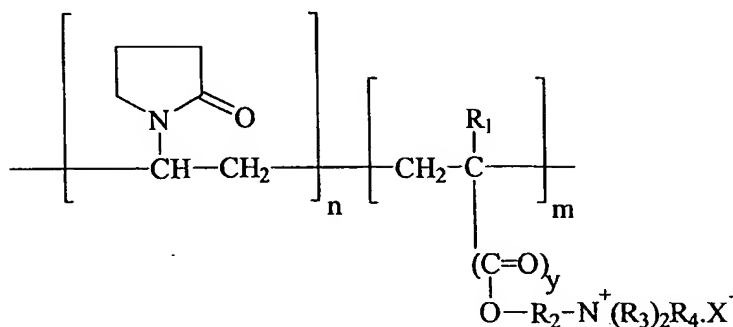
have a molecular weight of between 1,000 and 1,000,000, preferably between 10,000 and 500,000 and more preferably between 10,000 and 200,000.

For example particularly suitable N-vinylimidazole N-vinylpyrrolidone polymers for use herein have an average molecular weight range from 5,000-1,000,000, preferably from 5,000 to 500,000, and more preferably from 10,000 to 200,000. The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Such copolymers of N-vinylpyrrolidone and alkylallyl unsaturated monomers like PVP/vinyl acetate copolymers are commercially available under the trade name Luviskol® series from BASF.

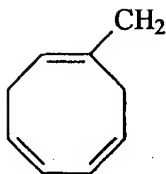
- Particular preferred copolymers of vinylpyrrolidone for use in the compositions of the present invention are quaternized or unquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers.

The vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers (quaternised or unquaternised) suitable for use in the compositions of the present invention are according to the following formula:



- in which n is between 20 and 99 and preferably between 40 and 90 mol% and m is between 1 and 80 and preferably between 5 and 40 mol%; R₁ represents H or CH₃; y denotes 0 or 1; R₂ is -CH₂-CHOH-CH₂- or C_xH_{2x}, in which x=2 to 18; R₃ represents a lower alkyl group of from 1 to 4 carbon atoms, preferably methyl or ethyl, or

8



R₄ denotes a lower alkyl group of from 1 to 4 carbon atoms, preferably methyl or ethyl; X⁻ is chosen from the group consisting of Cl, Br, I, 1/2SO₄, HSO₄ and CH₃SO₃. The polymers can be prepared by the process described in French Pat. Nos. 2,077,143 and 2,393,573.

The preferred quaternized or unquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers for use herein have a molecular weight of between 1,000 and 1,000,000, preferably between 10,000 and 500,000 and more preferably between 10,000 and 100,000.

Such vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers are commercially available under the name copolymer 845®, Gafquat 734®, or Gafquat 755® from ISP Corporation, New York, NY and Montreal, Canada or from BASF under the tradename Luviquat®.

Most preferred herein is quaternized copolymers of vinyl pyrrolidone and dimethyl aminoethylmethacrylate (polyquaternium-11) available from BASF.

20

The present invention is based on the finding that the liquid compositions of the present invention provide improved next-time cleaning performance when a hard-surface has been first treated therewith. Although not wishing to be bound by theory, it is speculated that the first antiresoiling ingredient, i.e., polyalkoxyethylene glycol diester, and the second antiresoiling ingredient, i.e., vinylpyrrolidone homopolymer or copolymer, have in common the property of adsorbing to a hard-surface being first cleaned therewith, in such a manner that a hygroscopic layer is left behind. The resulting hygroscopic layer can attract and retain ambient atmospheric water vapor to more effectively reduce adhesion of soils once treated and/or facilitate removal of soils subsequently deposited thereon, i.e. less work (e.g. less scrubbing and/or wiping and/or less chemical action) is required to remove the soils in the next-time cleaning operation, as compared to a similar soiled hard-surface which has been first

30

cleaned with the same compositions without the first or second antiresoiling ingredients according to the present invention.

5 More particularly, it has surprisingly been found that there is a synergistic effect on next-time cleaning performance associated with the use of such a polyalkoxyethylene glycol diester and a vinylpyrrolidone homopolymer or copolymer, as defined herein. Indeed, the next-time cleaning performance delivered by combining a polyalkoxyethylene glycol diester and a vinylpyrrolidone homopolymer or copolymer, as defined herein, in a liquid composition, is superior than the
10 next-time cleaning performance delivered by for example the same composition, but comprising only one of those ingredients at the same total level of antiresoiling ingredients.

15 In a preferred embodiment of the compositions of the present invention the polyalkoxyethylene glycol diester as defined herein, and the vinylpyrrolidone homopolymer or copolymer, as defined herein, are present at a weight ratio of the polyalkoxyethylene glycol diester to the vinylpyrrolidone homopolymer or copolymer of from 1:100 to 100:1, preferably from 1:10 to 10:1 and more preferably from 1:2 to 2:1.

20

Also an advantage of the present invention is that effective next-time cleaning performance can be obtained at low total level of antiresoiling ingredients. In a preferred embodiment the compositions herein comprise from 0.1% to 10% by weight of the total composition of the polyalkoxyethylene glycol diester, and the
25 vinylpyrrolidone homopolymer or copolymer, preferably from 0.2% to 5%, more preferably from 0.3% to 2% and most preferably from 0.3% to 1.5%. Surprisingly, effective next-time cleaning performance is delivered not only when a composition of the present invention is contacted to the hard-surface to clean in its neat form, but also in its diluted form, e.g. up to a dilution level
30 water: composition (400:1).

An advantage of the compositions of the present invention is that the first time cleaning performance is also increased, as compared for example to the same compositions without said vinylpyrrolidone homopolymer or copolymer.

35

By "cleaning performance", it is meant herein cleaning on various types of soils including greasy soils, like kitchen grease or burnt/sticky food residues typically found in a kitchen (e.g., burnt milk) and the like.

- 5 The first time dilute cleaning performance may be evaluated by the following test method: Tiles of enamel, vinyl or ceramic are prepared by applying to them a representative grease/particulate artificial soil, followed by aging. The test compositions and the reference composition are diluted (e.g., composition:water 1:50 or 1:100), applied to a sponge, and used to clean the
10 tiles with a Sheen scrub tester. The number of strokes required to clean to 100% clean is recorded. A minimum of 6 replicates can be taken with each result being generated in duplicate against the reference on each soiled tile.

- The next-time dilute cleaning performance may be evaluated by the following
15 test method: Following the procedure detailed for first time cleaning the tiles used for this previous test are taken and resoiled directly without first being further washed or rinsed. The cleaning procedure is then repeated using the Sheen scrub tester, taking care that the test compositions are used to clean the same part of the tile as was previously cleaned by them. The number of
20 strokes required to clean to 100% clean is recorded. A minimum of 6 replicates can be taken with each result being generated in duplicate against the reference on each soiled tile. This resoiling and cleaning procedure can be repeated up to 5 times.

- 25 The test method for evaluating neat cleaning performance is identical to above except that the test compositions and reference are used undiluted and that after cleaning a rinsing cycle is performed with clean water. This rinsing cycle may be repeated up to 5 times prior to the resoiling step for next time cleaning evaluation.

30

- Another advantage of the compositions of the present invention is that these compositions when applied on the surface to be cleaned either in their neat or diluted form dry faster than the same compositions comprising only the first or second antiresoiling ingredients as described herein at the same total level of
35 antiresoiling ingredients. Thus, the present invention also encompasses the use of a polyalkoxylene glycol diester and vinylpyrrolidone homopolymer or copolymer, in a liquid composition, for faster evaporation of said composition

when used to clean a hard-surface in its diluted or neat form, and/or faster evaporation of water subsequently coming into contact with said surface for rinsing off the surface after cleaning.

5 Although not wishing to be bound by theory, it has been observed that hard surfaces often have low affinity with water. This means that, when water gets in contact with hard-surfaces, its spreading, which is controlled by the interfacial energy (i.e., solid/liquid surface tension), is very limited. Indeed, it has been observed that the most stable configuration for water is grouping in spherical
10 droplets rather than forming a thin film uniformly spread over the surface. Thus requiring more time to completely evaporate from said surface. It has now been found that when the polyalkoxyethylene glycol diester and vinylpyrrolidone homopolymer or copolymer are added together into a liquid hard-surface cleaning composition according to the present invention a hydrophilic layer is
15 left on a hard-surface cleaned with said composition, said hydrophilic layer leaves the water coming in contact with the surface that has been first cleaned with said composition (e.g., water which is used to rinse off the surfaces having been so treated) uniformly spread over the surface ("sheeting effect") instead of forming droplets. This way, the evaporation of the composition itself and
20 subsequent water coming into contact with the surface for example in the rinsing step is accelerated.

Not to be bound by theory, it is believed that the antiresoiling ingredients described herein also have the ability to form a film on the surface of the user
25 skin, thereby providing improved skin mildness. In another embodiment, the present invention thus also encompasses the use of a polyalkoxyethylene glycol diester and/or polyvinyl pyrrolidone homopolymer or copolymer, in a liquid composition, for improved skin mildness.

30 An additional advantage related to the use of the polyalkoxyethylene glycol diester and/or polyvinyl pyrrolidone homopolymer or copolymer herein is that, as they adhere on hard surface making them more hydrophilic, the surfaces themselves become smoother (this can be perceived by touching said surfaces) and this contributes to convey perception of surface perfectly cleaned.

35

The compositions according to the present invention particularly suitable for the cleaning of a hard-surface are liquid compositions. The liquid compositions of

the present invention are preferably but not necessarily formulated as aqueous compositions. Aqueous compositions typically comprise from 50% to 99% by weight of the total composition of water, preferably from 60% to 95%, and more preferably from 80% to 95%.

5

The liquid compositions herein may be formulated in the full pH range of 0 to 14, preferably 1 to 13. Typically, the compositions herein are formulated in a neutral to highly alkaline pH range from 7 to 12, preferably from 9 to 11 and more preferably from 9.5 to 11. The pH of the compositions herein can be
10 adjusted by any of the means well-known to those skilled in the art such as acidifying agents like organic or inorganic acids, or alkalinising agents like NaOH, KOH, K₂CO₃, Na₂CO₃ and the like. Preferred organic acids for use herein have a pka of less than 6. Suitable organic acids are selected from the group consisting of citric acid, lactic acid, glycolic acid, succinic acid, glutaric
15 acid and adipic acid and mixtures thereof. A mixture of said acids may be commercially available from BASF under the trade name Sokalan® DCS.

Optional ingredients:

20 The liquid compositions according to the present invention may comprise a variety of optional ingredients depending on the technical benefit aimed for and the surface treated.

Suitable optional ingredients for use herein include surfactants, builders, chelants, polymers, solvents, buffers, bactericides, hydrotropes, colorants, stabilisers, radical scavengers, bleaches, bleach activators, suds controlling
25 agents like fatty acids, enzymes, soil suspenders, dye transfer agents, brighteners, anti dusting agents, dispersants, dye transfer inhibitors, pigments, dyes and/or perfumes.

30

Surfactants

The liquid compositions of the present invention preferably comprise a surfactant, or mixtures thereof. Said surfactant may be present in the
35 compositions according to the present invention in amounts of from 0.1% to 50% by weight of the total composition, preferably of from 0.1% to 20% and more preferably of from 1% to 10%.

Surfactants are desired herein as they further contribute to the cleaning performance and/or gloss benefit of the compositions of the present invention. Surfactants for use herein include nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof.

Particularly preferred surfactants are the nonionic surfactants. Suitable nonionic surfactants for use herein include a class of compounds which may be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be branched or linear aliphatic (e.g. Guerbet or secondary alcohols) or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. For example, a well-known class of nonionic synthetic detergents is made available on the market under the trade name "Pluronic". These compounds are formed by condensing ethylene oxide with an hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water-insolubility has a molecular weight of from about 1500 to 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water-solubility of the molecule as a whole and the liquid character of the products is retained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic detergents include :

- (i) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, and nonane;
- (ii) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine

products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. Examples are compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5000 to about 11000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2500 to 3000;

- 5
- (iii) The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms;
- 15 (iv) Trialkyl amine oxides and trialkyl phosphine oxides wherein one alkyl group ranges from 10 to 18 carbon atoms and two alkyl groups range from 1 to 3 carbon atoms; the alkyl groups can contain hydroxy substituents; specific examples are dodecyl di(2-hydroxyethyl)amine oxide and tetradecyl dimethyl phosphine oxide.
- 20 Also useful as a nonionic surfactant are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose, and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions of the preceding saccharide units.
- 30

Optionally, and less desirably, there can be a polyalkyleneoxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing

35

from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-
5 sides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-
sides and tallow alkyl tetra-, penta-, and hexagluco-
sides.

10

The preferred alkylpolyglycosides have the formula:



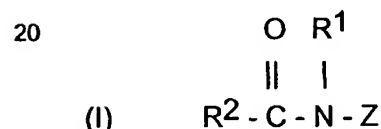
15 wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most
20 preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4-
25 and/or 6- position, preferably predominantly the 2- position.

Although not preferred, the condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use herein. The hydrophobic portion of
30 these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of
35 the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include

certain of the commercially available PluronicTM surfactants, marketed by BASF.

Also not preferred, although suitable for use as nonionic surfactants herein are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2,500 to about 3,000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Other suitable nonionic surfactants for use herein include polyhydroxy fatty acid amides of the structural formula :



wherein : R¹ is H, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxypropyl, or a mixture thereof, preferably C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R² is a C₅-C₃₁ hydrocarbyl, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₇ alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup can be utilised as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable

raw materials. Z preferably will be selected from the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$, $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$.

In Formula (I), R^1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

$\text{R}^2-\text{CO}-\text{N}<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructyl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

In one embodiment herein suitable nonionic surfactants for use herein are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C_8 - C_{14} alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C_8 - C_{18} alcohol ethoxylates (preferably C_{10} avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Particularly preferred surfactants include also the anionic surfactants. Suitable anionic surfactants for use herein include alkali metal (e.g., sodium or potassium) fatty acids, or soaps thereof, containing from about 8 to about 24, preferably from about 10 to about 20 carbon atoms.

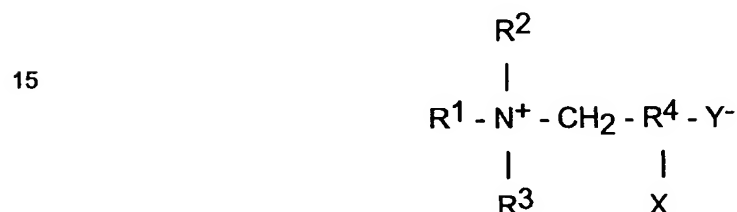
The fatty acids including those used in making the soaps can be obtained from natural sources such as, for instance, plant or animal-derived glycerides (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale oil, fish oil, tallow, grease, lard and mixtures thereof). The fatty acids can also be synthetically prepared (e.g., by oxidation of petroleum stocks or by the Fischer-Tropsch process). Alkali metal soaps can be made by direct saponification of fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soaps.

The term "tallow" is used herein in connection with fatty acid mixtures which typically have an approximate carbon chain length distribution of 2.5% C14, 29% C16, 23% C18, 2% palmitoleic, 41.5% oleic and 3% linoleic (the first three fatty acids listed are saturated). Other mixtures with similar distribution, such as the fatty acids derived from various animal tallows and lard, are also included within the term tallow. The tallow can also be hardened (i.e., hydrogenated) to convert part or all of the unsaturated fatty acid moieties to saturated fatty acid moieties. When the term "coconut" is used herein it refers to fatty acid mixtures which typically have an approximate carbon chain length distribution of about 8% C8, 7% C10, 48% C12, 17% C14, 9% C16, 2% C18, 7% oleic, and 2% linoleic (the first six fatty acids listed being saturated). Other sources having similar carbon chain length distribution such as palm kernel oil and babassu oil are included with the term coconut oil.

Other suitable anionic surfactants for use herein include water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in the molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Important examples of these synthetic detergents are the sodium, ammonium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, especially those of the types described in U.S. Pat. Nos. 2,220,099 and 2,477,383, incorporated herein by reference; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about three moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about four units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 carbon atoms; the reaction product of fatty acids esterified with isothionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of a methyl taurine in which the fatty acids, for example, are derived from coconut oil; and others known in the art, a number being specifically set forth in U.S.

Pat. Nos. 2,486,921, 2,486,922 and 2,396,278, incorporated herein by reference.

Suitable zwitterionic detergents for use herein comprise the betaine and
 5 betaine-like detergents wherein the molecule contains both basic and acidic
 groups which form an inner salt giving the molecule both cationic and anionic
 hydrophilic groups over a broad range of pH values. Some common examples
 of these detergents are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and
 2,255,082, incorporated herein by reference. Preferred zwitterionic detergent
 10 compounds have the formula:



20 wherein R1 is an alkyl radical containing from 8 to 22 carbon atoms, R2 and R3
 contain from 1 to 3 carbon atoms, R4 is an alkylene chain containing from 1 to
 3 carbon atoms, X is selected from the group consisting of hydrogen and a
 hydroxyl radical, Y is selected from the group consisting of carboxyl and
 sulfonyl radicals and wherein the sum of R1, R2 and R3 radicals is from 14 to
 25 24 carbon atoms.

Amphoteric and ampholytic detergents which can be either cationic or anionic
 depending upon the pH of the system are represented by detergents such as
 dodecylbeta-alanine, N-alkyltaurines such as the one prepared by reacting
 dodecylamine with sodium isethionate according to the teaching of U.S. Pat.
 30 No. 2,658,072, N-higher alkylaspartic acids such as those produced according
 to the teaching of U.S. Pat. No. 2,438,091, and the products sold under the
 trade name "Miranol", and described in U.S. Pat. No. 2,528,378, said patents
 being incorporated herein by reference. Additional synthetic detergents and
 listings of their commercial sources can be found in McCutcheon's Detergents
 35 and Emulsifiers, North American Ed. 1980, incorporated herein by reference.

Suitable amphoteric surfactants include the amine oxides corresponding to the formula:



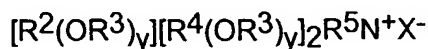
- 5 wherein R is a primary alkyl group containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R'' are, each, independently, an alkyl group containing 1 to 6 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. The preferred amine oxides are those in which the primary alkyl group has a straight chain in at least most of the molecules, generally at least 70%, preferably at least 90% of the molecules, and the amine oxides which are especially preferred are those in which R contains 10-18 carbons and R' and R'' are both methyl. Exemplary of the preferred amine oxides are the N-hexyldimethylamine oxide, N-octyldimethylamine oxide, N-decyldimethylamine oxide, N-dodecyl dimethylamine oxide, N-tetradecyldimethylamine oxide, N-hexadecyl dimethylamine oxide, N-octadecyldimethylamine oxide, N-eicosyldimethylamine oxide, N-docosyldimethylamine oxide, N-tetracosyl dimethylamine oxide, the corresponding amine oxides in which one or both of the methyl groups are replaced with ethyl or 2-hydroxyethyl groups and mixtures thereof. A most preferred amine oxide for use herein is N-decyldimethylamine oxide.

Other suitable amphoteric surfactants for the purpose of the invention are the phosphine or sulfoxide surfactants of formula:



- 25 wherein A is phosphorus or sulfur atom, R is a primary alkyl group containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R'' are, each, independently selected from methyl, ethyl and 2-hydroxyethyl. The arrow in the formula is a conventional representation of a semi-polar bond.

- Cationic surfactants suitable for use in compositions of the present invention are those having a long-chain hydrocarbonyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula:



wherein R^2 is an alkyl or alkyl benzyl group having from 8 to 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

Perfumes

Suitable perfumes for use herein include materials which provide an olfactory aesthetic benefit and/or cover any "chemical" odour that the product may have. The main function of a small fraction of the highly volatile, low boiling (having low boiling points), perfume components in these perfumes is to improve the fragrance odor of the product itself, rather than impacting on the subsequent odor of the surface being cleaned. However, some of the less volatile, high boiling perfume ingredients provide a fresh and clean impression to the surfaces, and it is desirable that these ingredients be deposited and present on the dry surface. Perfume ingredients can be readily solubilized in the compositions, for instance by the nonionic detergent surfactants. The perfume ingredients and compositions suitable to be used herein are the conventional ones known in the art. Selection of any perfume component, or amount of perfume, is based solely on aesthetic considerations.

Suitable perfume compounds and compositions can be found in the art including U.S. Pat. Nos. : 4,145,184, Brain and Cummins, issued March 20, 1979; 4,209,417, Whyte, issued June 24, 1980; 4,515,705, Moeddel, issued May 7, 1985; and 4,152,272, Young, issued May 1, 1979, all of said patents being incorporated herein by reference. In general, the degree of substantivity of

a perfume is roughly proportional to the percentages of substantive perfume material used. Relatively substantive perfumes contain at least about 1%, preferably at least about 10%, substantive perfume materials. Substantive perfume materials are those odorous compounds that deposit on surfaces via the cleaning process and are detectable by people with normal olfactory acuity. Such materials typically have vapour pressures lower than that of the average perfume material. Also, they typically have molecular weights of about 200 and above, and are detectable at levels below those of the average perfume material. Perfume ingredients useful herein, along with their odor character, and their physical and chemical properties, such as boiling point and molecular weight, are given in "Perfume and Flavor Chemicals (Aroma Chemicals)," Steffen Arctander, published by the author, 1969, incorporated herein by reference.

Examples of the highly volatile, low boiling, perfume ingredients are : anethole, benzaldehyde, benzyl acetate, benzyl alcohol, benzyl formate, iso-bornyl acetate, camphene, ciscitral (neral), citronellal, citronellol, citronellyl acetate, para-cymene, decanal, dihydrolinalool, dihydromyrcenol, dimethyl phenyl carbinol, eucaliptol, geranial, geraniol, geranyl acetate, geranyl nitrile, cis-3-hexenyl acetate, hydroxycitronellal, d-limonene, linalool, linalool oxide, linalyl acetate, linalyl propionate, methyl anthranilate, alpha-methyl ionone, methyl nonyl acetaldehyde, methyl phenyl carbonyl acetate, laevo-menthyl acetate, menthone, iso-menthone, mycrene, myrcenyl acetate, myrcenol, nerol, neryl acetate, nonyl acetate, phenyl ethyl alcohol, alpha-pinene, beta-pinene, gamma-terpinene, alpha-terpineol, beta-terpineol, terpinyl acetate, and vertenex (para-tertiary-butyl cyclohexyl acetate). Some natural oils also contain large percentages of highly volatile perfume ingredients. For example, lavandin contains as major components : linalool; linalyl acetate; geraniol; and citronellol. Lemon oil and orange terpenes both contain about 95% of d-limonene.

Examples of moderately volatile perfume ingredients are : amyl cinnamic aldehyde, iso-amyl salicylate, beta-caryophyllene, cedrene, cinnamic alcohol, coumarin, dimethyl benzyl carbonyl acetate, ethyl vanillin, eugenol, iso-eugenol, flor acetate, heliotropine, 3-cis-hexenyl salicylate, hexyl salicylate, lilial (para-tertiarybutyl-alpha-methyl hydrocinnamic aldehyde), gamma-methyl ionone, nerolidol, patchouli alcohol, phenyl hexanol, beta-selinene, trichloromethyl phenyl carbonyl acetate, triethyl citrate, vanillin, and veratraldehyde. Cedarwood terpenes are composed mainly of alpha-cedrene, beta-cedrene, and other C₁₅H₂₄ sesquiterpenes.

Examples of the less volatile, high boiling, perfume ingredients are : benzophenone, benzyl salicylate, ethylene brassylate, galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gama-2-benzopyran), hexyl cinnamic aldehyde, lylal (4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-10-carboxaldehyde), methyl cedrylone, methyl dihydro jasmonate, methyl-beta-naphthyl ketone, musk indanone, musk ketone, musk tibetene, and phenylethyl phenyl acetate.

Selection of any particular perfume ingredient is primarily dictated by aesthetic considerations.

The compositions herein may comprise a perfume ingredient, or mixtures thereof, in amounts up to 5.0% by weight of the total composition, preferably in amounts of 0.1% to 1.5%.

15 Chelating agents

Another class of optional compounds for use herein include chelating agents or mixtures thereof. Chelating agents can be incorporated in the compositions herein in amounts ranging from 0.0% to 10.0% by weight of the total composition, preferably 0.1% to 5.0%.

Suitable phosphonate chelating agents for use herein may include alkali metal ethane 1-hydroxy diphosphonates (HEDP), alkylene poly (alkylene phosphonate), as well as amino phosphonate compounds, including amino aminotri(methylene phosphonic acid) (ATMP), nitrilo trimethylene phosphonates (NTP), ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates (DTPMP). The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonate (DTPMP) and ethane 1-hydroxy diphosphonate (HEDP). Such phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST®.

Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to

Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

5 A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'- disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N'- disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4, 704, 233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N'- disuccinic acids is, for instance, commercially available
10 under the tradename ssEDDS® from Palmer Research Laboratories.

Suitable amino carboxylates for use herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA),N- hydroxyethylethylenediamine triacetates, nitrilotri-acetates,
15 ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, ethanol-diglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine di-acetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium, and substituted ammonium salt forms. Particularly suitable amino carboxylates to be used herein are diethylene triamine penta acetic acid, propylene diamine
20 tetracetic acid (PDTA) which is, for instance, commercially available from BASF under the trade name Trilon FS® and methyl glycine di-acetic acid (MGDA).

Further carboxylate chelating agents for use herein include salicylic acid, aspartic acid, glutamic acid, glycine, malonic acid or mixtures thereof.

25

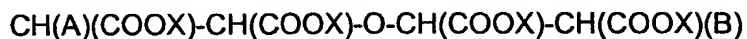
Builders:

The liquid compositions of the present invention may also comprises a builder or a mixture thereof, as an optional ingredient. Suitable builders for use herein
30 include polycarboxylates and polyphosphates, and salts thereof. Typically, the compositions of the present invention comprise up to 20.0 % by weight of the total composition of a builder or mixtures thereof, preferably from 0.1% to 10.0% , and more preferably from 0.5% to 5.0%.

35 Suitable and preferred polycarboxylates for use herein are organic polycarboxylates where the highest LogKa, measured at 25°C/0.1M ionic strength is between 3 and 8, wherein the sum of the LogKCa + LogKMg,

measured at 25°C/0.1M ionic strength is higher than 4, and wherein $\text{LogKCa} = \text{LogKMg} \pm 2$ units, measured at 25°C/0.1M ionic strength.

Such suitable and preferred polycarboxylates include citrate and complexes of
5 the formula:

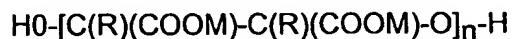


wherein A is H or OH; B is H or $-\text{O-CH(COOX)-CH}_2(\text{COOX})$; and X is H or a
10 salt-forming cation. For example, if in the above general formula A and B are both H, then the compound is oxydisuccinic acid and its water-soluble salts. If A is OH and B is H, then the compound is tartrate monosuccinic acid (TMS) and its water-soluble salts. If A is H and B is $-\text{O-CH(COOX)-CH}_2(\text{COOX})$, then the compound is tartrate disuccinic acid (TDS) and its water-soluble salts.
15 Mixtures of these builders are especially preferred for use herein. Particularly TMS to TDS, these builders are disclosed in U.S. Patent 4,663,071, issued to Bush et al., on May 5, 1987.

Still other ether polycarboxylates suitable for use herein include copolymers of
20 maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulfonic acid.

Other useful polycarboxylate builders include the ether hydroxypolycarboxylates represented by the structure :

25



wherein M is hydrogen or a cation wherein the resultant salt is water-soluble, preferably an alkali metal, ammonium or substituted ammonium cation, n is
30 from about 2 to about 15 (preferably n is from about 2 to about 10, more preferably n averages from about 2 to about 4) and each R is the same or different and selected from hydrogen, C_{1-4} alkyl or C_{1-4} substituted alkyl (preferably R is hydrogen).

35 Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679;

3,835,163; 4,158,635; 4,120,874 and 4,102,903, all of which are incorporated herein by reference.

5 Preferred amongst those cyclic compounds are dipicolinic acid and chelidanic acid.

Also suitable polycarboxylates for use herein are mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, benzenene pentacarboxylic acid, and carboxymethyloxysuccinic acid, and soluble salts thereof.

10

Still suitable carboxylate builders herein include the carboxylated carbohydrates disclosed in U.S. Patent 3,723,322, Diehl, issued March 28, 1973, incorporated herein by reference.

15

Other suitable carboxylates for use herein, but which are less preferred because they do not meet the above criteria are alkali metal, ammonium and substituted ammonium salts of polyacetic acids. Examples of polyacetic acid builder salts are sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine, tetraacetic acid and nitrilotriacetic acid.

20

Other suitable, but less preferred polycarboxylates are those also known as alkyliminoacetic builders such as methyl imino diacetic acid, alanine diacetic acid, methyl glycine diacetic acid, hydroxy propylene imino diacetic acid and other alkyl imino acetic acid builders.

25

Also suitable in the compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanediotes and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986, incorporated herein by reference. Useful succinic acid builders include the C5-C20 alkyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Alkyl succinic acids typically are of the general formula $R-CH(COOH)CH_2(COOH)$ i.e., derivatives of succinic acid, wherein R is hydrocarbon, e.g., C₁₀-C₂₀ alkyl or alkenyl, preferably C₁₂-C₁₆ or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents, all as described in the above-mentioned patents.

35

The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts.

Specific examples of succinate builders include : laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0 200 263, published November 5, 1986.

Examples of useful builders also include sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentane-tetracarboxylate, water-soluble polyacrylates and the copolymers of maleic anhydride with vinyl methyl ether or ethylene.

Other suitable polycarboxylates are the polyacetal carboxylates disclosed in U.S. Patent 4,144,226, Crutchfield et al., issued March 13, 1979, incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together, under polymerization conditions, an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

Polycarboxylate builders are also disclosed in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

Suitable polyphosphonates for use herein are the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates. The most preferred builder for use herein is citrate.

Divalent ions:

The compositions according to the present invention may further comprise a divalent ion, or mixtures thereof. All divalent ions known to those skilled in the art may be used herein. Preferred divalent ions to be used herein are calcium, zinc, cadmium, nickel, copper, cobalt, zirconium, chromium and/or magnesium and more preferred are calcium, zinc and/or magnesium. Said divalent ions may be added in the form of salts for example as chloride, acetate, sulphate, formate and/or nitrate or as a complex metal salt. For example, calcium may be added in the form of calcium chloride, magnesium as magnesium acetate or magnesium sulphate and zinc as zinc chloride. Typically such ions may be present at a level up to 3 %, preferably from 0.001% to 1% by weight of the total composition.

Other antiresoiling ingredients:

The compositions of the present invention particularly suitable for the cleaning of a hard-surface may comprise another antiresoiling ingredient on top of the polyalkoxyethylene glycol diester and polyvinyl homopolymer or copolymer as described herein before. Suitable additional antiresoiling ingredients for use herein include those selected from the group consisting of polyalkoxyethylene glycol, mono- and dicapped polyalkoxyethylene glycol and a mixture thereof, as defined herein after. The compositions of the present invention may comprise up to 20% by weight of the total composition of such another antiresoiling ingredient or a mixture thereof, preferably from 0.01% to 10%, more preferably from 0.1% to 5% and most preferably from 0.2% to 2%.

Suitable polyalkoxyethylene glycols for use herein are according to the following formula $\text{H-O}-(\text{CH}_2\text{-CHR}_2\text{O})_n\text{-H}$.

Suitable monocapped polyalkoxyethylene glycols for use herein are according to the following formula $\text{R}_1\text{-O}-(\text{CH}_2\text{-CHR}_2\text{O})_n\text{-H}$.

Suitable dicapped polyalkoxyethylene glycols for use herein are according to the formula $\text{R}_1\text{-O}-(\text{CH}_2\text{-CHR}_2\text{O})_n\text{-R}_3$.

In these formulas the substituents R_1 and R_3 each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched

hydrocarbon chains having from 1 to 30 carbon atoms, or amino bearing linear or branched, substituted or unsubstituted hydrocarbon chains having from 1 to 30 carbon atoms, R_2 is hydrogen or a linear or branched hydrocarbon chain having from 1 to 30 carbon atoms, and n is an integer greater than 0.

5

Preferably R_1 and R_3 each independently are substituted or unsubstituted, linear or branched alkyl groups, alkenyl groups or aryl groups having from 1 to 30 carbon atoms, preferably from 1 to 16, more preferably from 1 to 8 and most preferably from 1 to 4, or amino bearing linear or branched, substituted or
10 unsubstituted alkyl groups, alkenyl groups or aryl groups having from 1 to 30 carbon atoms, more preferably from 1 to 16, even more preferably from 1 to 8 and most preferably from 1 to 4. Preferably R_2 is hydrogen, or a linear or branched alkyl group, alkenyl group or aryl group having from 1 to 30 carbon atoms, more preferably from 1 to 16, even more preferably from 1 to 8, and
15 most preferably R_2 is methyl, or hydrogen. Preferably n is an integer greater than 1, more preferably from 5 to 1000, more preferably from 10 to 100, even more preferably from 20 to 60 and most preferably from 30 to 50.

The preferred polyalkoxyethylene glycols, mono and dicapped polyalkoxyethylene
20 glycols to be used herein have a molecular weight of at least 200, more preferably from 400 to 5000 and most preferably from 800 to 3000.

Suitable monocapped polyalkoxyethylene glycols for use herein include 2-aminopropyl polyethylene glycol (MW 2000), methyl polyethylene glycol (MW
25 1800) and the like. Such monocapped polyalkoxyethylene glycols may be commercially available from Hoescht under the polyglycol series or Hunstman under the tradename XTJ®. Suitable polyalkoxyethylene glycols to be used herein are polyethylene glycols like polyethylene glycol (MW 2000).

Suitable dicapped polyalkoxyethylene glycols for use herein include O,O'-bis(2-aminopropyl)polyethylene glycol (MW 2000), O,O'-bis(2-aminopropyl)polyethylene glycol (MW 400), O,O'-dimethyl polyethylene glycol (MW 2000), dimethyl polyethylene glycol (MW 2000), or mixtures thereof. A preferred dicapped polyalkoxyethylene glycol for use herein is dimethyl
30 polyethylene glycol (MW 2000). For instance dimethyl polyethylene glycol may be commercially available from Hoescht as the polyglycol series, e.g. PEG DME-2000, or from Huntsman under the name Jeffamine® and XTJ®.
35

These polyalkoxyethylene glycols, mono- or dicapped polyalkoxyethylene glycols contribute to the benefit of the liquid hard-surface compositions of the present invention, i.e. they help further improving the next-time cleaning performance of the composition herein. Dicapped polyalkoxyethylene glycols are highly preferred herein.

Suds controlling agents:

- 10 The compositions according to the present invention may further comprise a suds controlling agent such as 2-alkyl alkanol, or mixtures thereof, as a preferred optional ingredient. Particularly suitable to be used in the present invention are the 2-alkyl alkanols having an alkyl chain comprising from 6 to 16 carbon atoms, preferably from 8 to 12 and a terminal hydroxy group, said alkyl chain being substituted in the α position by an alkyl chain comprising from 1 to 15 10 carbon atoms, preferably from 2 to 8 and more preferably 3 to 6. Such suitable compounds are commercially available, for instance, in the Isofol® series such as Isofol® 12 (2-butyl octanol) or Isofol® 16 (2-hexyl decanol).
- 20 Other suds controlling agents may include alkali metal (e.g., sodium or potassium) fatty acids, or soaps thereof, containing from about 8 to about 24, preferably from about 10 to about 20 carbon atoms.

The fatty acids including those used in making the soaps can be obtained from natural sources such as, for instance, plant or animal-derived glycerides (e.g., 25 palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale oil, fish oil, tallow, grease, lard and mixtures thereof). The fatty acids can also be synthetically prepared (e.g., by oxidation of petroleum stocks or by the Fischer-Tropsch process). Alkali metal soaps can be made by direct saponification of 30 fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soaps. The term "tallow" is used herein in connection with fatty acid mixtures which typically have an approximate carbon chain length distribution of 2.5% C14, 29% C16, 23% C18, 35 2% palmitoleic, 41.5% oleic and 3% linoleic (the first three fatty acids listed are saturated). Other mixtures with similar distribution, such as the fatty acids

derived from various animal tallows and lard, are also included within the term tallow. The tallow can also be hardened (i.e., hydrogenated) to convert part or all of the unsaturated fatty acid moieties to saturated fatty acid moieties. When the term "coconut" is used herein it refers to fatty acid mixtures which typically
5 have an approximate carbon chain length distribution of about 8% C8, 7% C10, 48% C12, 17% C14, 9% C16, 2% C18, 7% oleic, and 2% linoleic (the first six fatty acids listed being saturated). Other sources having similar carbon chain length distribution such as palm kernel oil and babassu oil are included with the term coconut oil.

10

Other suitable suds controlling agents are exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various
15 types. These materials can be incorporated as particulates in which the suds controlling agent is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds controlling agent can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other
20 components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds controlling agents are the self-emulsifying silicone suds controlling agents, described in German Patent
25 Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer.

Especially preferred silicone suds controlling agents are described in
30 Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^R.

Especially preferred suds controlling agent are the suds controlling agent
35 system comprising a mixture of silicone oils and the 2-alkyl-alcanols.

Typically, the compositions herein may comprise up to 4% by weight of the total composition of a suds controlling agent, or mixtures thereof, preferably from 0.1% to 1.5% and most preferably from 0.1% to 0.8%.

5 Solvents

The compositions of the present invention may further comprise a solvent or a mixtures thereof. Solvents for use herein include all those known to the those skilled in the art of hard-surfaces cleaner compositions. Suitable solvents for
10 use herein include ethers and diethers having from 4 to 14 carbon atoms, preferably from 6 to 12 carbon atoms, and more preferably from 8 to 10 carbon atoms, glycols or alkoxyated glycols, alkoxyated aromatic alcohols, aromatic alcohols, aliphatic branched alcohols, alkoxyated aliphatic branched alcohols, alkoxyated linear C1-C5 alcohols, linear C1-C5 alcohols, C8-C14 alkyl and
15 cycloalkyl hydrocarbons and halohydrocarbons, C6-C16 glycol ethers and mixtures thereof.

Suitable glycols to be used herein are according to the formula HO-CR₁R₂-OH wherein R₁ and R₂ are independently H or a C₂-C₁₀ saturated or unsaturated
20 aliphatic hydrocarbon chain and/or cyclic. Suitable glycols to be used herein are dodecaneglycol and/or propanediol.

Suitable alkoxyated glycols to be used herein are according to the formula R-(A)_n-R₁-OH wherein R is H, OH, a linear saturated or unsaturated alkyl of from
25 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein R₁ is H or a linear saturated or unsaturated alkyl of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, and A is an alkoxy group preferably ethoxy, methoxy, and/or propoxy and n is from 1 to 5, preferably 1 to 2. Suitable alkoxyated glycols to be used herein are methoxy
30 octadecanol and/or ethoxyethoxyethanol.

Suitable alkoxyated aromatic alcohols to be used herein are according to the formula R (A)_n-OH wherein R is an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more
35 preferably from 2 to 10, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2.

Suitable alkoxyated aromatic alcohols are benzoxyethanol and/or benzoxypropanol.

5 Suitable aromatic alcohols to be used herein are according to the formula R-OH wherein R is an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 1 to 15 and more preferably from 1 to 10. For example a suitable aromatic alcohol to be used herein is benzyl alcohol.

10 Suitable aliphatic branched alcohols to be used herein are according to the formula R-OH wherein R is a branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 5 to 12. Particularly suitable aliphatic branched alcohols to be used herein include 2-ethylbutanol and/or 2-methylbutanol.

15 Suitable alkoxyated aliphatic branched alcohols to be used herein are according to the formula R (A)_n-OH wherein R is a branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 5 to 12, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1
20 to 2. Suitable alkoxyated aliphatic branched alcohols include 1-methylpropoxyethanol and/or 2-methylbutoxyethanol.

Suitable alkoxyated linear C1-C5 alcohols to be used herein are according to the formula R (A)_n-OH wherein R is a linear saturated or unsaturated alkyl
25 group of from 1 to 5 carbon atoms, preferably from 2 to 4, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Suitable alkoxyated aliphatic linear C1-C5 alcohols are butoxy propoxy propanol (n-BPP), butoxyethanol, butoxypropanol, ethoxyethanol or mixtures thereof. Butoxy propoxy propanol is commercially
30 available under the trade name n-BPP® from Dow chemical.

Suitable linear C1-C5 alcohols to be used herein are according to the formula R-OH wherein R is a linear saturated or unsaturated alkyl group of from 1 to 5 carbon atoms, preferably from 2 to 4. Suitable linear C1-C5 alcohols are
35 methanol, ethanol, propanol or mixtures thereof.

Other suitable solvents include butyl diglycol ether (BDGE), butyltriglycol ether, ter amilic alcohol and the like. Particularly preferred solvents to be used herein are butoxy propoxy propanol, butyl diglycol ether, benzyl alcohol, butoxypropanol, ethanol, methanol, isopropanol and mixtures thereof.

5

Typically, the compositions of the present invention comprise up to 20% by weight of the total composition of a solvent or mixtures thereof, preferably from 0.5% to 10% by weight and more preferably from 1% to 8%.

10 Bleaching components

The liquid compositions herein may also comprise a bleaching component. Any bleach known to those skilled in the art may be suitable to be used herein including any peroxygen bleach as well as a chlorine releasing component.

15

Suitable peroxygen bleaches for use herein include hydrogen peroxide or sources thereof. As used herein a source of hydrogen peroxide refers to any compound which produces active oxygen when said compound is in contact with water. Suitable water-soluble sources of hydrogen peroxide for use herein
20 include percarbonates, preformed percarboxylic acids, persilicates, persulphates, perborates, organic and inorganic peroxides and/or hydroperoxides.

25

Suitable chlorine releasing component for use herein is an alkali metal hypochlorite. Advantageously, the composition of the invention are stable in presence of this bleaching component. Although alkali metal hypochlorites are preferred, other hypochlorite compounds may also be used herein and can be selected from calcium and magnesium hypochlorite. A preferred alkali metal hypochlorite for use herein is sodium hypochlorite.

30

Bleach activators

35 The compositions of the present invention that comprise a peroxygen bleach may further comprise a bleach activator or mixtures thereof. By "bleach activator", it is meant herein a compound which reacts with peroxygen bleach

like hydrogen peroxide to form a peracid. The peracid thus formed constitutes the activated bleach. Suitable bleach activators to be used herein include those belonging to the class of esters, amides, imides, or anhydrides. Examples of suitable compounds of this type are disclosed in British Patent GB 1 586 769 and GB 2 143 231 and a method for their formation into a prilled form is described in European Published Patent Application EP-A-62 523. Suitable examples of such compounds to be used herein are tetracetyl ethylene diamine (TAED), sodium 3,5,5 trimethyl hexanoyloxybenzene sulphonate, diperoxy dodecanoic acid as described for instance in US 4 818 425 and nonylamide of peroxyadipic acid as described for instance in US 4 259 201 and n-nonanoyloxybenzenesulphonate (NOBS). Also suitable are N-acyl caprolactams selected from the group consisting of substituted or unsubstituted benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, hexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, formyl caprolactam, acetyl caprolactam, propanoyl caprolactam, butanoyl caprolactam pentanoyl caprolactam or mixtures thereof. A particular family of bleach activators of interest was disclosed in EP 624 154, and particularly preferred in that family is acetyl triethyl citrate (ATC). Acetyl triethyl citrate has the advantage that it is environmental-friendly as it eventually degrades into citric acid and alcohol. Furthermore, acetyl triethyl citrate has a good hydrolytical stability in the product upon storage and it is an efficient bleach activator. Finally, it provides good building capacity to the composition.

Packaging form of the compositions

25

The compositions herein may be packaged in a variety of suitable detergent packaging known to those skilled in the art. The liquid compositions are preferably packaged in conventional detergent plastic bottles.

30 In one embodiment the compositions herein may be packaged in manually operated spray dispensing containers, which are usually made of synthetic organic polymeric plastic materials. Accordingly, the present invention also encompasses liquid cleaning compositions of the invention packaged in a spray dispenser, preferably in a trigger spray dispenser or pump spray dispenser.

35

Indeed, said spray-type dispensers allow to uniformly apply to a relatively large area of a surface to be cleaned the liquid cleaning compositions suitable for use

according to the present invention. Such spray-type dispensers are particularly suitable to clean vertical surfaces.

Suitable spray-type dispensers to be used according to the present invention include manually operated foam trigger-type dispensers sold for example by Specialty Packaging Products, Inc. or Continental Sprayers, Inc. These types of dispensers are disclosed, for instance, in US-4,701,311 to Dunning et al. and US-4,646,973 and US-4,538,745 both to Focarracci. Particularly preferred to be used herein are spray-type dispensers such as T 8500® commercially available from Continental Spray International or T 8100® commercially available from Canyon, Northern Ireland. In such a dispenser the liquid composition is divided in fine liquid droplets resulting in a spray that is directed onto the surface to be treated. Indeed, in such a spray-type dispenser the composition contained in the body of said dispenser is directed through the spray-type dispenser head via energy communicated to a pumping mechanism by the user as said user activates said pumping mechanism. More particularly, in said spray-type dispenser head the composition is forced against an obstacle, e.g. a grid or a cone or the like, thereby providing shocks to help atomise the liquid composition, i.e. to help the formation of liquid droplets.

20

The process of cleaning a hard-surface:

The present invention also encompasses a process of cleaning hard-surfaces wherein a liquid composition comprising a polyalkoxyethylene glycol diester and a vinylpyrrolidone homopolymer or copolymer as described herein before, is contacted with said surfaces.

By "hard-surfaces", it is meant herein any kind of surfaces typically found in houses like kitchens, bathrooms, or in car interiors or exteriors, e.g., floors, walls, tiles, windows, sinks, showers, shower plastified curtains, wash basins, WCs, dishes, fixtures and fittings and the like made of different materials like ceramic, vinyl, no-wax vinyl, linoleum, melamine, glass, any plastics, plastified wood, metal or any painted or varnished or sealed surface and the like. Hard-surfaces also include household appliances including, but not limited to, refrigerators, freezers, washing machines, automatic dryers, ovens, microwave ovens, dishwashers and so on.

35

The liquid compositions of the present invention may be contacted to the surface to be cleaned in its neat form or in its diluted form.

5 By "diluted form" it is meant herein that said liquid composition is diluted by the user typically with water. The composition is diluted prior use to a typical dilution level of 10 to 400 times its weight of water, preferably from 10 to 200 and more preferably from 10 to 100. Usual recommended dilution level is a 1.2% dilution of the composition in water.

10 In the preferred process of cleaning hard-surfaces according to the present invention where said composition is used in diluted form, there is no need to rinse the surface after application of the composition in order to obtain excellent first and next-time cleaning performance and also excellent end result surface appearance.

15

The present invention will be further illustrated by the following examples.

20

Examples

The following compositions were made by mixing the listed ingredients in the listed proportions. All proportions are % by weight of the total composition. Excellent first and next-time cleaning performance and good gloss were delivered to the hard-surfaces cleaned with these compositions both under neat and diluted conditions, e.g. at a dilution level of 50:1 to 200:1 (water:composition).

25

Compositions (weight%):

	A	B	C	D	E	F
<u>Nonionic surfactants</u>						
C 9-11 EO5	2.4	1.9	2.5	-	-	2.5
C12,14 EO5	3.6	2.9	2.5	2.5	-	2.5
C7-9 EO6	-	-	-	-	3.2	-
Dobanol® 23-3	-	-	-	-	1.3	-
AO21	1.0	0.8	4.0	-	1.9	2.0
<u>Anionic surfactants</u>						
NaPS	-	-	-	-	-	-
NaLAS	-	-	-	4.0	0.9	0.8
NaCS	1.5	2.6	-	2.3	1.2	1.5
C8-AS	-	-	-	-	0.8	-
Isalchem® AS	0.6	0.6	-	-	-	-
<u>Buffer</u>						
Na ₂ CO ₃	0.6	0.13	0.6	1.0	1.0	0.1
Citrate	0.5	0.56	0.5	-	-	0.6
Caustic	0.3	0.33	0.3	-	-	0.3
<u>Suds control</u>						
Fatty Acid	0.6	0.3	0.5	0.4	0.4	0.5
Isofol 12®	0.3	0.3	-	0.3	0.3	0.3
<u>Polymers</u>						
Kessco 6000DS®	0.4	-	0.3	-	0.5	0.35
Marlosol FS®	-	0.4	-	0.5	-	-
PVP K60®	-	-	-	0.5	-	-
PVP K90®	0.3	0.4	0.6	-	0.5	0.3
Minors and water	——	——	up	to	100%	——
pH	9.5	7.4	9.5	10.5	10.75	7.5

	G	H	I	J	K	L	M
<u>Nonionic surfactants</u>							
C 9-11 EO5	-	-	2.5	2.4	-	2.5	0.030
C12,14 EO5	-	-	2.5	3.6	-	2.5	0.030
C7-9 EO6	3.2	8	-	-	3.2	-	-
Dobanol® 23-3	1.3	3.2	-	-	1.3	-	-
AO21	1.9	4.8	2.0	1.0	1.9	2.0	0.024
<u>Anionic surfactants</u>							
NaPS	-	3.0	-	-	-	-	-
NaLAS	0.9	-	0.8	-	0.9	0.8	0.009
NaCS	1.2	3.0	1.5	1.5	1.2	1.5	0.018
C8-AS	0.8	2.0	-	-	0.8	-	-
Isalchem® AS	-	-	-	0.6	-	-	-
<u>Buffer</u>							
Na ₂ CO ₃	1.0	2.0	0.2	0.6	1.0	0.2	0.002
Citrate	-	-	0.75	0.5	-	0.75	0.009
Caustic	-	-	0.5	0.3	-	0.5	0.006
<u>Suds control</u>							
Fatty Acid	0.4	0.8	0.4	0.6	0.4	0.4	0.005
Isofol 12®	0.3	-	0.3	0.3	0.3	0.3	0.004
<u>Polymers</u>							
Kessco 6000DS®	0.5	0.75	0.5	0.5	0.5	0.4	0.006
PVP K90®	-	0.5	0.5	-	-	0.3	0.006
PVP K60®	0.5	-	-	0.5	0.5	-	-
<u>Minors and water</u>							
pH	—	— up	to	100%	—	—	—
	10.7	10.75	9.5	9.5	10.75	9.5	8.5

PVP K60® and PVP K90® are vinylpyrrolidone homopolymers (average molecular weight of 160,000), commercially available from ISP Corporation, New York, NY and Montreal, Canada.

5 Kessco 6000DS® is O,O'- distearyl polyethylene glycol diester commercially available from Akzo Nobel.

Marlosol FS® is O,O'-dioleoyl polyethylene glycol diester commercially available from Huls.

Isofol 12® is 2-butyl octanol

10 Dobanol® 23-3 is a C12-C13 EO 3 nonionic surfactant commercially available from SHELL.

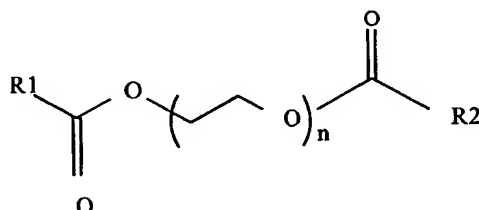
C8-AS is octyl sulphate available from Albright and Wilson, under the tradename Empimin® LV 33.

AO21 is a C12-14 EO21 alcohol ethoxylate.

15 Isalchem® AS is a branched alcohol alkyl sulphate commercially available from Enichem.

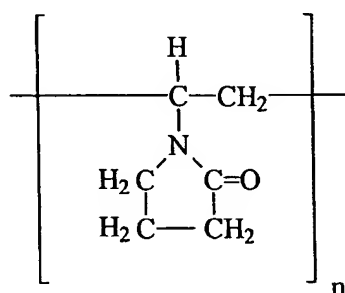
Claims

1. A liquid hard-surface cleaning composition comprising a polyalkoxyene glycol diester according to the formula:



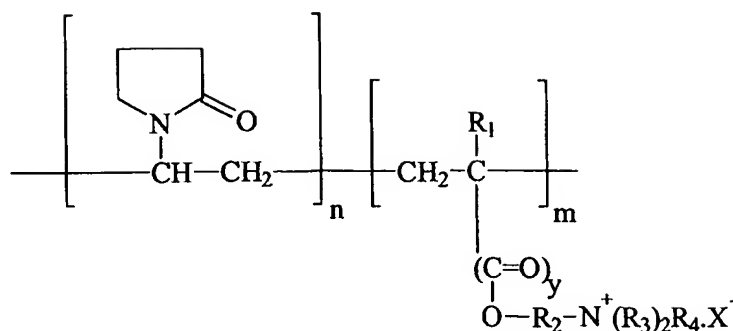
- wherein the substituents R_1 and R_2 each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chains having from 1 to 36 carbon atoms and wherein n is an integer from 10 to 400, and a vinylpyrrolidone homopolymer or copolymer.
2. A composition according to claim 1 which comprises from 0.001% to 20% by weight of the total composition of the polyalkoxyene glycol diester or a mixture thereof, preferably from 0.01% to 10%, more preferably from 0.1% to 5% and even more preferably from 0.2% to 2%.
3. A composition according to any of the preceding claims wherein in said polyalkoxyene glycol diester, the substituents R_1 and R_2 each independently are substituted or unsubstituted, linear or branched alkyl groups or alkenyl groups having from 1 to 36 carbon atoms, preferably from 1 to 30, more preferably from 1 to 24, even more preferably from 1 to 22 and most preferably from 1 to 18, or aryl groups having up to 36 carbon atoms, preferably from 6 to 36, more preferably from 6 to 30, and wherein n is an integer from 20 to 400, more preferably from 40 to 300, even more preferably from 40 to 200 and most preferably from 40 to 150.
4. A composition according to any of the preceding claims wherein said polyalkoxyene glycol diester is O,O'-distearyl polyethylene glycol diester, O,O'-dioleyl polyethylene glycol diester or a mixture thereof.

5. A composition according to any of the preceding claims which comprises from 0.001% to 20% by weight of the total composition of vinylpyrrolidone homopolymer or copolymer or a mixture thereof, preferably from 0.01% to 10%, more preferably from 0.1% to 5% and even more preferably from 0.2% to 2%.
6. A composition according to any of the preceding claims wherein said vinylpyrrolidone homopolymer is an homopolymer of N-vinylpyrrolidone having the following repeating monomer:

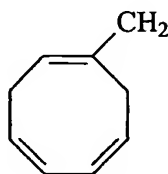


wherein n is an integer of from 10 to 1,000,000, preferably 20 to 100,000 and more preferably from 20 to 10,000.

7. A composition according to any of the preceding claims wherein said vinylpyrrolidone copolymer is a copolymer of N-vinylpyrrolidone and alkylenically unsaturated monomer preferably selected from the group consisting of maleic acid, chloromaleic acid, fumaric acid, itaconic acid, citraconic acid, phenylmaleic acid, aconitic acid, acrylic acid, N-vinylimidazole, vinyl acetate, and anhydrides thereof, styrene, sulphonated styrene, alpha-methyl styrene, vinyl toluene, t-butyl styrene and mixtures thereof.
8. A composition according to any of the preceding claims wherein said vinylpyrrolidone copolymer is a quaternized or unquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymer according to the following formula:



in which n is between 20 and 99 and preferably between 40 and 90 mol% and m is between 1 and 80 and preferably between 5 and 40 mol%; R_1 represents H or CH_3 ; y denotes 0 or 1; R_2 is $-\text{CH}_2-\text{CHOH}-\text{CH}_2-$ or C_xH_{2x} , in which $x=2$ to 18; R_3 represents a lower alkyl group of from 1 to 4 carbon atoms, preferably methyl or ethyl, or



R_4 denotes a lower alkyl group of from 1 to 4 carbon atoms, preferably methyl or ethyl; X^- is chosen from the group consisting of Cl, Br, I, $1/2\text{SO}_4$, HSO_4 and CH_3SO_3 .

9. A composition according to any of the preceding claims wherein said vinylpyrrolidone copolymer is a quaternized copolymer of vinylpyrrolidone and dimethylaminoethylmethacrylate.
10. A composition according to any of the preceding claims which is an aqueous liquid composition having a pH of from 1 to 13, preferably of from 7 to 12 and more preferably of from 9 to 11.
11. A composition according to any of the preceding claims which further comprises an optional ingredient selected from the group consisting of surfactants, builders, chelants, polymers, solvents, buffers, bactericides, hydrotropes, colorants, stabilisers, radical scavengers, bleaches, bleach activators, fatty acids, enzymes, soil suspenders, dye transfer agents,

brighteners, anti dusting agents, suds controlling agents, dispersants, dye transfer inhibitors, pigments, dyes, perfumes and mixtures thereof.

12. A composition according to claim 11 wherein said surfactant is selected from the group consisting of nonionic surfactants, anionic surfactants, zwitterionic surfactants, amphoteric surfactants, cationic surfactants and mixtures thereof and is present at a level of from 0.1% to 50% by weight of the total composition, preferably from 0.1% to 20% and more preferably from 1% to 10%.
13. A process of cleaning a hard-surface wherein a liquid composition according to any of the preceding claims, is contacted with said surface.
14. A process of cleaning a hard-surface according to claim 13 wherein said composition is contacted with said surface after having been diluted with water.
15. A process according to claim 14 wherein said surface is not rinsed after said composition has been contacted with said surface.
16. The use, of a polyalkoxylene glycol diester and a vinylpyrrolidone homopolymer or copolymer, in a liquid composition, for faster evaporation of said composition when used to clean a hard-surface in its diluted or neat form, and/or for faster evaporation of water subsequently coming into contact with said surface typically for rinsing off the surface after having been cleaned with said composition.

INTERNATIONAL SEARCH REPORT

In tional Application No

PCT/US 98/21677

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D1/74 C11D3/37 C11D1/72

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 673 569 A (S.L.SHERNOV ET AL.) 16 June 1987 see the whole document	1,10-12
A	EP 0 635 567 A (RECKITT & COLMAN INC.) 25 January 1995 cited in the application see claims	1,6
A	WO 95 07336 A (PROCTER & GAMBLE) 16 March 1995 see claims	1
A	GB 1 450 234 A (KAO CORP) 22 September 1976 see claims	1
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

8 February 1999

Date of mailing of the international search report

17/02/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Pelli Wablat, B

INTERNATIONAL SEARCH REPORT

In tional Application No

PCT/US 98/21677

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 06900 A (COLGATE PALMOLIVE CO) 31 March 1994 see claims 1,8 ---	1
A	DATABASE WPI Section Ch, Week 9336 Derwent Publications Ltd., London, GB; Class A97, AN 93-285603 XP002061290 & JP 05 202382 A (LION CORP) , 10 August 1993 see abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

In tional Application No

PCT/US 98/21677

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4673569 A	16-06-1987	NONE	
EP 0635567 A	25-01-1995	NONE	
WO 9507336 A	16-03-1995	US 5451341 A AU 7829794 A BR 9407442 A CA 2170484 A CN 1133608 A CZ 9600713 A EP 0717770 A HU 74044 A JP 9502472 T ZA 9406908 A	19-09-1995 27-03-1995 09-04-1996 16-03-1995 16-10-1996 14-08-1996 26-06-1996 28-10-1996 11-03-1997 20-04-1995
GB 1450234 A	22-09-1976	NONE	
WO 9406900 A	31-03-1994	AU 4856693 A EP 0660872 A MX 9305581 A US 5593614 A ZA 9306280 A	12-04-1994 05-07-1995 29-07-1994 14-01-1997 26-05-1995